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Multi-L1₀ domain CoPt and FePt nanoparticles revealed by electron microscopy

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Although it has recently attracted a considerable attention, the structure of bi-metallic magnetic nanoparticles such as CoPt or FePt is still debated. These nanoalloys are promising for applications, in particular due to the extremely high magnetocrystalline anisotropy (MCA) of the bulk face-centered tetragonal (fct) L1₀ phase where pure atomic Co (or Fe) and Pt planes are stacked along the [001] direction. At small sizes, these systems appear to be much more complex than single element metallic particles: in addition to the usual existence of peculiar symmetries (icosahedral and decahedral) when the size is reduced, the various possibilities of chemical ordering offer another degree of freedom [1]. Despite this increased complexity, several theoretical investigations have tackled this question, predicting for nanoparticles smaller than 3 nm the stability (or metastability) of exotic structures displaying at the same time a five-fold symmetry and a chemical order [2-4]. However, evidence of few nanometers chemically-ordered particles retaining a five-fold symmetry is still missing.

We discuss the atomic structure of CoPt and FePt nanoparticles (with a diameter between 2 nm and 5 nm), synthesized by the mass-selected low-energy cluster-beam deposition technique. For both alloys, we show using transmission electron microscopy (TEM) that crystalline nanocrystals coexist with multiply-twinned particles (MTP) having decahedral or icosahedral symmetries. In particular, we show that the chemical order can be preserved across twin boundaries which can give rise to spectacular chemically ordered decahedral particles made of five L1₀ domains, as theoretically predicted [2-4]. The samples have been characterized by TEM either in a high resolution mode (HRTEM) or with a high angle annular dark field detector in a scanning TEM mode (STEM-HAADF). In addition to a JEOL 2010F microscope (operating at 200 kV and with a field emission gun), we have used FEI Titan 80-300 microscopes operating at 300 kV with a field emission gun, either with a C_s-corrector for the objective lens (for HRTEM images with highly improved spatial resolution) or with an aberration corrected probe (for atomic resolution STEM-HAADF images).

The three types of particle structure (fcc crystal, decahedron, icosahedron) can be observed, both for CoPt and FePt. These experimental observations indicate that, in this size range, the energy differences between the different types of clusters are smaller or of the order of the thermal energy. Both for FePt and CoPt, we observe crystalline particles with a single chemically ordered L1₀ domain all along the nanoparticle, down to D = 2.3 nm (smallest diameter considered here). In the present case we do not observe any threshold size. Moreover, there is no indication of a preferential surface segregation of one element. Remarkably, we also observe a chemical order in crystalline particles consisting of several L1₀ domains. In some cases, the different **c**-orientations are due to (111) twins (see Fig. 1a-b) which can preserve a coherent chemical order. Even more surprisingly, it is also possible to find different L1₀ domains in a 2 nm CoPt particle free of twins (Z-contrast image, see Fig. 1c-d). In this case, one domain has a **c** axis at 90° with respect from two other domains that are joined by an antiphase boundary (APB).

Finally, as illustrated in Fig. 2, particles showing a striking pentagonal pattern can also be found. They consist in decahedral clusters made of five L1₀ domains joined by (111) twins (see Fig. 2b). Multislice images simulations have been performed, considering a particle with a perfect chemical order, and are in excellent agreement with the experimental C_s-corrected HRTEM images (Fig. 3). This remarkable particle structure is precisely the one predicted by theoretical calculations [2-4]. From a magnetic point of view, it is expected that the MCA of these decahedral particles will be very

low, despite they are exclusively formed of $L1_0$ ordered domains. In the same way, for crystalline particles, twinning and coexistence of several domains having different c orientations will certainly drastically reduce the MCA as compared to mono- $L1_0$ domain fct particles [5].

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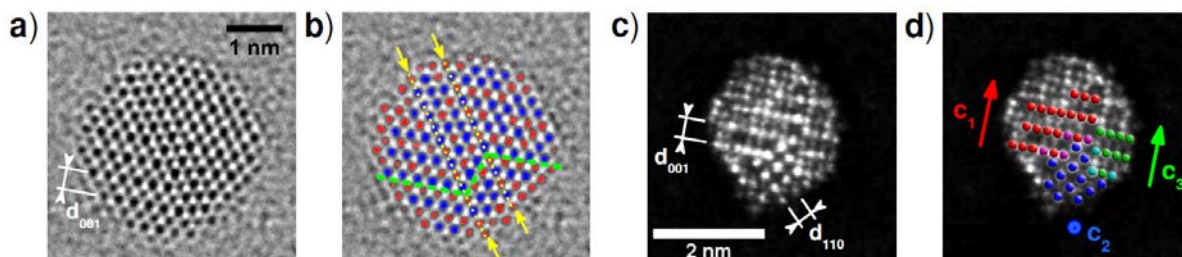


Figure 1. a) C_s -corrected HRTEM image of a CoPt particle displaying a continuous $L1_0$ chemical order over two (111) twins (indicated by arrows in b). As a guide to the eyes, in b) the atomic columns are colored according to their apparent size in the original image. c) STEM-HAADF image of another CoPt particle: the bright dots correspond to Pt-rich atomic columns. Three different $L1_0$ domains can be distinguished, as schematized in d).

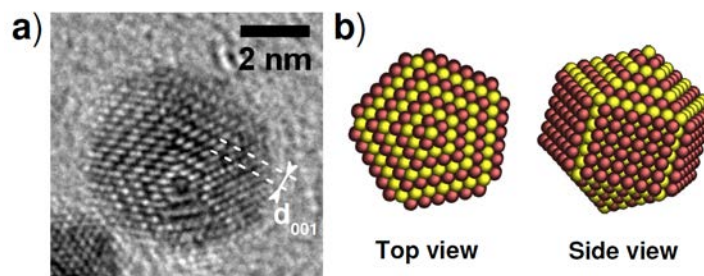


Figure 2. a) HRTEM image of a FePt particle displaying simultaneously a five-fold symmetry and $L1_0$ ordered domains. b) schematic view of the corresponding chemically ordered decahedral structure, predicted by theoretical calculations.

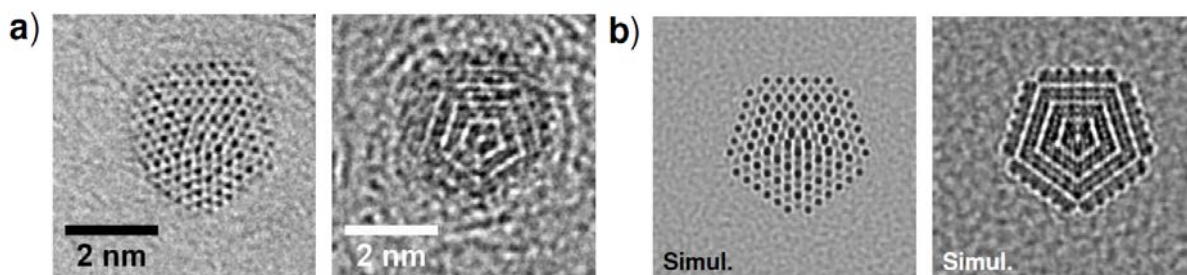


Figure 3. a) C_s -corrected experimental HRTEM images of a chemically ordered decahedral FePt particle, for two defocus values. b) Multislice image simulation, using the geometry shown in Fig. 2b, with Fe atoms at the center.